METHOD OF APPLYING METAL COATINGS ON PARTICLES AND SUBSTRATES..

Technical Field

The present invention relates to the technology of applying metal coatings on the surfaces of various materials (particles and substrates) including dielectrics, semiconductors and metals. The invention can be used, for example, for the metallization of abrasive particles, in applying metal coating to ceramic materials and in electronics.

Background Art

The techniques conventionally used for applying metal coatings on the surfaces of materials include chemical vapor-phase deposition, plasma assisted deposition, metal bath deposition, electroless deposition, electrolytic deposition and solid-phase reaction techniques.

The technique of vapor-phase deposition (patents US 5 250 086, US 5 232 469, US 5 224 969, US 5 126 207, US 5 024 680, US 4 399 167, US 3 924 031, US 3 871 840, US 3 650 714) uses gaseous mixtures at low pressures and high substrate temperatures for the deposition of carbide-forming metals, such as chromium, titanium and zirconium. For example, patent US 5 224 969 describes a process in which a layer of fine chromium powder is mixed with the diamond and heated to elevated temperatures (600-700 °C) under 10^{-6} torr vacuum (or in the atmosphere of argon or hydrogen). During the process agitation is applied in order to prevent the particles from adhering to one another. The treatment causes the metal powder to vaporize and redeposit on the surfaces of the diamond powder forming metal carbide. The drawbacks of this technique include the use of elevated temperatures (600-700 °C) which causes diamond degradation, the use of expensive carbide-forming metals, the necessity to apply a second layer of metals which are more oxidation resistant and the necessity to apply agitation in order to prevent the particles from adhering to one another.

Plasma assisted deposition technique (US 5 489 449) allows one to obtain an adherent

metal coating on a flat dielectric substrate. In the case of coating a powder it is necessary to create fluidized bed conditions in order to prevent particles from adhering to one another. This causes high expenditure of purified gases, especially if the particles are relatively large (more than 40 μm). Other disadvantages of the technique include the use of elevated temperatures, expensive reactors, high expenditure of oxygen-free gas and short lifetime of the electrodes.

In the technique of packed salt bath deposition (US 5 250 086, US 5 224 969, US 5 306 318, US 5 090 969) abrasive particles are immersed within a molten bath of one or more alkali or alkaline earth halides with a carbide-forming metal, such as chromium, titanium, tungsten, zirconium, vanadium, niobium, tantalum, molybdenum, the process operating at 600 - 100 °C, for chromium, preferrably, between 800-950 °C (US 5 250 086). Patent US 5 306 318 describes the process of coating particles of cubic boron nitride with titanium; patent US 5 090 969 describes the use of molten alkali metal ftoride for the metallization of diamond and cubic boron nitride. The disadvantages of the technique include the use of elevated temperatures (600-700 °C), which causes diamond degradation, the use of expensive carbide-forming metals, the necessity to apply a second layer of metals which are more oxidation resistant and the necessity to apply agitation in order to prevent the particles from adhering to one another. The melts containing titanium (US 3 929 432) and titanium hydrides (US 4 591 363) have been described. Mechanical crushing of sintered particles aggregates is needed in this case, which leads to appearance of uncoated areas, cracks and other defects.

In the electrolytic method (US 5 421 989) dielectric materials first must be coated with a layer of metal by means of other techniques. The technique does not have the drawbacks of the described above methods and is characterized by high productivity; however, in case of powders containing up to 50 w. % of metal the quality of the metal coating obtained is low.

Electroless technique (US 4 435 189, US 5 188 643, US 5 648 125. US 5 221 328, US 4 997 686, US 4 520 052) comprises degreasing, cleaning, activation and sensibilization of the surface of a dielectric material with a subsequent reducing of a metal on the surface from the metal salt solution. The process is slow; increasing metal content in the solution

leads to segregation of coarse metal particles and the coated material; the degree of coverage is low (coverage coefficient 50-70 %) which can be explained by the low density of metal crystallization centers on the surface of the dielectric material. In this technique it is difficult to control the thickness of the metal layer.

Solid-phase reactions are utilized in the process of coating in a number of patents (US 4 063 907, US 5 256 443, EP 0 513 821, EP 0 508 399). Patent US 4 063 907 describes a process in which mechanical treatment of abrasive particles and metal compounds is used, with a metal compound being able to be decomposed or reduced at atmospheric pressure and temperatures 800-1400 °C, e.g. molibdenium, tungsten, titanium, niobium, tantalum, chromium and zirconium sulfides. The use of high temperatures and low degree of coverage of the material are disadvantages of the technique. Patent EP 0 513 821 describes a process in which a thin film of solution containing a noble metal alkoxide is deposited on the surface of a substrate, dried and heated in a reducing atmosphere in order to obtain a thin film of noble metals and/or in oxidizing atmosphere in order to obtain a thin film of noble metal oxides. Patent 5 256 443 describes a process in which a sol containing noble metal alkoxides is prepared, and a thin film is dried until a gel is formed. The technique does not permit to obtain a thick adherent coating; the reagents (metal alkoxides and palladium salts) are expensive.

Patent EP 0 508 399, which is the closest analog of the present invention (prototype), describes a process in which a substrate and an organic salt of a metal are heated to temperatures not higher than 400 °C at low pressure in the presence of palladium salts. Pyrolysis of the organic salt of metal takes place, and the products of the pyrolysis form the necessary coating on the substrate.

Disadvantages of the prototype process (EP 0 508 399) are following:

1. It is impossible to obtain a coating which would be dense, adherent and thick, because a substantial amount of gaseous products is formed during decomposition of the organic salts of metals, which leads to porosity and low adherence of the coating.
2. If this method is applied to powder dielectric materials, it is laborious and expensive, as in this case it is necessary to agitate the powder during the process of pyrolysis of the organic salt of metal by means of creation of the fluidized bed conditions or by

means of pulverization and drying. If this process is not performed, mechanical crushing of sintered particles aggregates is needed in this case, which leads to appearance of uncoated areas, cracks and other defects. This is a common drawback of all methods comprising mechanical crushing of sintered aggregates (patents US 3 929 432, US 4 591 363).

3. The reagents (organic salts of metals and palladium salts) are expensive.

Disclosure of Invention

The goal of the present invention is to obtain a dense adherent coating with a controlled thickness on the surface of various materials which are able to withstand heating to 200-500 °C (diamond, abrasives, ceramics, glass, dielectrics, semiconductors, metals), the coating having high degree of coverage and the process being highly productive and inexpensive.

The goal is achieved in the following way: after degreasing and cleaning of the surface of materials, the particles of a compound chosen from the group of metals, alloys, metal oxides, metal hydroxides, metal sulfides (metals are copper, nickel, aluminum, zinc, titanium, tungsten, germanium, gold, cobalt, molybdenum, tin, palladium, platinum) are mechanically smeared on the surface of the material with a subsequent reducing of the compound in non-oxidizing atmosphere on heating to 200-500 °C.

In contrast to the process described in the prototype patent EP 0 508 399, said inorganic compounds release small amounts of gaseous products of decomposition, which allows one to obtain a dense adherent coating with a high degree of coverage. The thickness and degree of coverage were estimated by the technique of X-ray diffraction (see Mode 1). Adherence of the obtained coating was estimated by means of comparison of the X-ray diffraction patterns of the metallized powder before and after treatment in an ultrasonic bath (see Mode 3). The described technique is less laborious and less expensive than the prototype as its application to the coating of powders does not require neither fluidized bed conditions nor pulverization and drying; expensive reagents such as palladium salts and organic salts of metals are not needed.

desired thickness and degree of coverage; 100 % degree of coverage can be achieved. The method is also advantageous in that the process is performed at relatively low temperatures and does not require neither equipment of complicated design nor expensive reagents, the process has high productivity and it can be organized in such a way that it has no waste products. The metal coating obtained has a rough surface, which provides good retention of metallized abrasive grains both in metal and organic matrixes of abrasive instruments.

The present invention is explained below in more detail by reference to the following Modes, but the invention is not construed as being limited thereto.

Modes for Carrying Out the Invention.

Mode 1. (Best mode)

After degreasing, cleaning and drying, synthetic diamond powder (particle size 50 μm) was mixed with copper dioxide (diamond/copper weight ratio 1:1). Mixing balls (diameter 5 mm), which had been previously treated (fettled) by copper dioxide, were put in the mixer; the ratio of the masses of mixture and mixing balls was 2:1. The process of mixing took 20 min. The mixture was heated to 450 °C in the atmosphere of oxygen-free dry argon. The end of the gas release indicated the end of the process. After cooling the powder was treated by CF_2Cl_2 and dried. Productivity in this case was 3 kg/hr for the reactor of 6 liters.

The degree of coverage and the thickness were estimated with the help of X-ray diffraction technique. The depth of penetration of CuKα radiation in a copper sample is more than 3 μm. The diffraction maximums corresponding to the structure of diamond were not observed in the X-ray diffraction pattern of the dimond powder coated with copper. Thus, a conclusion can be made that the thickness of the coating is more than 3 μm and the degree of coverage is 100 % (the accuracy of the measurements is 0.5 %).

Mode 2.

Degreasing of the surface is usually performed in an alkaline solution. Cleaning of the surface can be performed by etching in dilute acid or by other methods, for example, by laser treatment of the surface of the substrate (S.M. Pimenov, G.A. Shafeev, V.A. Laptev, E.N. Loubnin, Appl. Phys. Lett., 64 (15) 1994, p. 1935-1937). The materials which can be coated by means of the described process are: synthetic and natural diamond, cubic boron nitride, corundum, ruby, sapphire, silicon carbide, fianite, ceramics, glass, semiconductors and other materials that are able to withstand heating to said temperatures.

Coating may contain copper, nickel, aluminum, zinc, titanium, tungsten, germanium, gold, cobalt, molybdenum, tin, palladium, platinum and their alloys. Mechanical smearing of the particles, which would form coating, is achieved by mixing in various mills and mixers. If the surface to be coated is flat, one has to spread the particles on the surface by rolling or by pouring a suspension with a high content of the solid phase with a subsequent drying and rolling. A substrate having a complex shape can be treated with the help of pulverization of a suspension or of a powder.

The compounds that serve to form a coating are monoxide and dioxide of copper, monoxide of nickel, oxides, hydroxides and sulfides of said metals. One can also use metal powder. Reduction can be performed in the atmosphere of argon, purified nitrogen or hydrogen or at low pressure (10^{-3} torr). The value of the maximum temperature of heating depends upon the nature and degree of purification of the gas used, upon the pressure maintained and upon the compound used for coating. When hydrogen or other oxygen-free dry gas or vacuum (10^{-3} torr) are applied, it is necessary to heat to 200-500 °C. One or several layers of the metal coating can be deposited by means of the described technique or by other methods on the metal coating obtained. The metal coating obtained can be protected from oxidation by treatment in organic solvents (CF_2Cl_2, $CHClF_2$ or CF_4). Sometimes it is necessary to obtain a layer of metal oxide on a substrate or on a powder. In this case the metal layer obtained is heated in oxidizing atmosphere till the required degree of oxidation is attained.

The metal coating produced by the described method is characterized by high density and high value of adhesion to the surface of the coated material; one can obtain a coating of

After degreasing, cleaning and drying, powder of cubic boron nitride (particles of 50-60 μm) was immersed in an aluminum suspension. The suspension had been obtained by means of mixing aluminum powder in a solvent containing water and ethanol for 15-30 min. The solvent was then evaporated at 100 °C and the mixture was heated in a closed reactor at temperatures 250-300 °C. After cooling the powder was treated by $CHClF_2$ and dried. The degree of coverage was estimated by the technique of X-ray diffraction and was found to be 90-95 % (the accuracy of determination was 0.5 %).

Mode 3.

After degreasing, cleaning and drying, corundum powder (Al_2O_3, particles size 60-80 μm) was immersed in a titanium suspension. The suspension had been obtained by mixing of titanium powder in a solution containing water and ethanol for 15-30 min. The solvent was then evaporated at 100 °C and the mixture was heated in a closed reactor at temperatures 250-300 °C. After cooling the powder was treated by CF_4 and dried.

Adherence of the coating was estimated by comparison of the X-ray diffraction data obtained before and after treatment of the metallized powder in an ultrasonic bath at frequency 20 kHz for 3 min. No difference between the X-ray diffraction spectra of the metallized powder before and after ultrasonic treatment was found, which is an evidence of a high value of adhesion at the metal/dielectric boundary.

Mode 4.

A ceramic plate containing zirconium dioxide was degreased, cleaned and dried. A suspension of high solid phase content was poured on the surface of the plate to form a film of 10 μm. The suspension had been prepared by mixing nickel monoxide (90 %), polyvinilbutiral, plastifier and stabilizer in a mill containing milling balls. After drying the plate was heated in the atmosphere of dry hydrogen at 390 °C. Release of the calculated amount of water indicated the end of the process. After cooling the plate was treated in CF_2Cl_2 and dried.

Industrial application.

The invention can be used in industry in applying metal coatings on the surfaces of various materials (particles and substrates) including dielectrics, semiconductors and metals. It can be used, for example, in manufacturing of abrasive tools for the metallization of abrasive particles, in automotive industry for producing metal-matrix composites, in applying metal coating to ceramic materials and in electronics in manufacturing of such devices as heat sinks, circuit boards, resistors, electrodes, sensors and magnetic media.

Claims.

1. A method of applying a metal coating on the surface of materials (powders and substrates) which comprises degreasing, cleaning and drying of the surface and mechanical smearing of the particles of a compound chosen from the group of metals, alloys, metal oxides, metal hydroxides, metal sulfides (metals are copper, nickel, aluminum, zinc, titanium, tungsten, germanium, gold, cobalt, molybdenum, tin, palladium, platinum) on the surface of the material with a subsequent reducing of the compound on heating in non-oxidizing atmosphere.
2. A method as claimed in claim 1, wherein said mechanical smearing of said particles on powders is carried out with the help of mixing in mills and mixers.
3. A method as claimed in claim 1, wherein said mechanical smearing of said particles on flat surfaces is carried out by rolling or by pouring a high solid phase content suspension with a subsequent drying and rolling.
4. A method as claimed in claim 1, wherein said mechanical smearing of said particles on the surface of a substrate having a complex shape is carried out with the help of pulverization of a suspension or of a powder.
5. A method as claimed in claim 1, wherein copper monoxide and dioxide and nickel monoxide are used as said compounds which form the metal coating, and heating is performed in non-oxidizing atmosphere to temperatures 200-500 °C.
6. A method as claimed in claim 1, wherein said mechanical smearing of said metals and alloys is performed in non-oxidizing atmosphere to temperatures 200-300 °C.
7. A method as claimed in claim 1, wherein one or several secondary layers of metal are applied to the surface of the primary metal layer and/or metal layer is protected from oxidation by treatment in organic solvents (CF_2Cl_2, $CHClF_2$ or CF_4).
8. A method as claimed in claim 1, wherein metal layer obtained is heated in an oxidizing atmosphere until the required degree of oxidation is obtained.
9. A method as claimed in claim 1, wherein the material to be coated is an abrasive powder (synthetic or natural diamond, cubic boron nitride, corundum, ruby, sapphire, silicon carbide).
10. A method as claimed in claim 1, wherein metallized abrasive particles are sintered with metal by the technique of hot pressing in an inert atmosphere in order to obtain a compact for manufacturing of an abrasive instrument.

11. A method as claimed in claim 1, wherein said material with a metal coating is an element of an electronic device.

PATENT COOPERATION TREAT

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

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in its capacity as elected Office

Date of mailing (day/month/year) 19 June 2000 (19.06.00)	
International application No. PCT/RU99/00254	**Applicant's or agent's file reference** 11111102
International filing date (day/month/year) 14 July 1999 (14.07.99)	**Priority date** (day/month/year) 17 July 1998 (17.07.98)
Applicant FOKINA, Elena Leonidovna et al	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

14 July 1999 (14.07.99)

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PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 11111102	**FOR FUTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No PCT/RU 99/00254	International filing date (day/month/year) 14 July 1999(14.07.99)	Priority date (day/month/year) 17 July 1998 (17.07.98)
International Patent Classification (IPC) or national classification and IPC	C23C 24/08	
Applicant FOKINA Elena Leonidovna et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant accoding to Article 36

2. This Report consists of a total of 3 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claimes and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70/16 and Section 607 of the Administrative Instructions under PCT).

These annexes consist of a total of _____ sheets

3. This report contains indications relating to the following items:

I ☒ Basis of the report

II ☐ Priority

III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

IV ☐ Lack of unity of invention

V ☒ Reasoned statement under Articl 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

VI ☐ Certain documents cited

VII ☐ Certain defects in the international application

VIII ☐ Certain observations on the international application

Date of submission of the demand: 14 July 1999 (14.07.99)	Date of completion of this report: 18 May 2000 (18.05.2000)
Name and mailing address of the IPEA/ RU Federal institut of industrial property Russia, 121858,Moscow,Berezhkovskaya nab., 30-1 Facsimile No.	Authorized officer I.Poimenova Telephone No 240-2591

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No
PCT/RU 99/00254

1. Basis of the report

1. With regard to the **elements** of the international application:*

☒ the international application as originally filed

☐ the description:

pages _____, as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____

☐ the claims:

pages _____, as originally filed
pages _____, as amended (together with any statement) under Article 19
pages _____, filed with the demand
pages _____, filed with the letter of _____

☐ the drawings:

pages _____, as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____

☐ the sequence listing part of the description:

pages _____, as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language _____ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3 (b)).
☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form
☐ furnished subsequently to this Authority in computer form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed been furnished.
☐ The statement that the information recorded in computer readable form is identical to the sequence listing has been furnished.

4. ☐ The amendments have resulted in the cancellation of:
☐ the description, pages _____
☐ the claims, Nos. _____
☐ the drawings, sheets/fig _____

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Bof (Rule 70.2(c)).**

* *Replacement sheets which have been furnished to the receiving Office in response to an iinvitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*

** *Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.*

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No
PCT/RU 99/00254

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicabillity; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1-11	YES
	Claims		NO
Inventive step (IS)	Claims	1-11	YES
	Claims		NO
Industrial applicability (IA)	Claims	1-11	YES
	Claims		NO

2. Citations and explanations (Rule 70.7)

Claims 1-11 meet the criteria of novelty and inventive step since documents cited in the search report don't disclose a method of applying a metal coating on the surface of materials in that mechanical smearing of the particles of a compound chosen from the group of metals, alloys, metall oxides, metal hydroxides, metal sulfides (metals are copper, nickel, aluminum, zinc, titanium, tungsten, germanium, gold, cobalt, molybdenum, tin, palladium, platinum) on the surface of the material with a subsequent reducing of the compound on heating in non-oxidizing atmosphere.

St. Petersburg, Russia

Fax number: (1-703) 305 3230

Fax to: Assistant Commissioner for Patents

Number of pages:

From: Galina G. Chernik

From Fax number 007 (812) 428 6919, e-mail chernik@nonel.pu.ru

January 11, 2001

Dear Sirs/Madames,

I am sending the documents to apply for a US patent as we have USA as a designated state in our application according to the PCT procedure.

Sincerely,

(G. G. Chernik)

Galina Chernik, PhD

PCT

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International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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A1

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98113972 17 July 1998 (17.07.98) RU

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Published
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Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: METHOD OF APPLYING METAL COATINGS ON PARTICLES AND SUBSTRATES

(57) Abstract

A method of applying dense adherent metal coatings on the surfaces of various materials (particles and substrates) including dielectrics, semiconductors and metals, is provided. The method utilizes solid–phase reactions. After degreasing and cleaning of the surface of materials, the particles of a compound chosen from the group of metals, alloys, metal oxides, metal hydroxides, metal sulfides are mechanically smeared on the surface of the material with a subsequent reducing of the compound in non–oxidizing atmosphere on heating to 200–500 °C.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/RU 99/00254

A. CLASSIFICATION OF SUBJECT MATTER

C23C 24/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C 24/00 - 24/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched:

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
A	SU 318314 A1 (I.M.VAISTUKH et al.) 7 January 1990 (07.01.90), abstract	1-11
A	EP 0297678 A1 (AKZO N.V.) 4 January 1989 (04.01.89), abstract	1-11
A	EP 0358829 A1 (POND, ROBERT B.,SR.) 21 March 1990 (21.03.90), abstract	1-11
A	SU 248421 A (N.V.AVDEEV et al.), 10 December 1969 (10.12.69)	1-11

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex

* Special categories of cited documents:

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" Y " document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search	Date of mailing of the international search report
15 December 1999 (15.12.99)	23 December 1999 (23.12.99)

Name and mailing address of the ISA/RU FIPS	Authorized officer
Russia, 121858, Moskva, Berezhkovskaya nab., 30-1	I.Poimenova
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